(6) No experimental evidence has been obtained which would warrant the conclusion that more than two allotropes of cadmium exist between the freezing and boiling temperatures of water.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY AND THE CHEMICAL LABORATORY OF VASSAR COLLEGE.]

THE MELTING POINTS OF THE CHLORIDES OF LITHIUM, RUBIDIUM AND CAESIUM, AND THE FREEZING POINTS OF BINARY AND TERNARY MIXTURES OF THESE SALTS, INCLUDING ALSO POTASSIUM AND SODIUM CHLORIDE.

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The work recorded below was incidental to another research, for which it was desired to obtain eutectic mixtures of alkali chlorides. Since, however, the main research may not be soon completed, it is perhaps worth while to record the following incidental and incomplete results—especially since they confirm the recently published results of Korreng in points where his work differs from that of earlier investigators.[1] The determinations recounted below were made during the winter of 1913–1914, before Korreng's work appeared.

Preparation of Materials.

Lithium Chloride.—For preliminary experiments a commercial sample, supposed to contain less than 0.1% of potassium and sodium, was employed; but it gave a melting point 12° lower than the much purer specimen used in the final determinations. This latter substance was prepared from exceedingly pure lithium nitrate (remaining from the Harvard work on the atomic weight of lithium)[2] by evaporating repeatedly with excess of hydrochloric acid in a quartz dish on an electric stove, finally fusing the salt in quartz in an atmosphere of hydrochloric acid gas.

Sodium Chloride.—A saturated solution of very pure sodium bicarbonate was neutralized with chemically pure hydrochloric acid. The solution was further saturated with hydrochloric acid and the salt precipitated. It was purified by reprecipitation.

Potassium Chloride.—"Chemically pure" potassium chloride from a competent firm was purified in a similar way by three precipitations with hydrochloric acid. Spectroscopic examination showed it to be free from sodium and other metals of the alkali group.

Rubidium Chloride.—Kahlbaum's salt, though free from other alkali metals, was found to contain rubidium nitrate in considerable quantity.

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[1] Korreng, *Z. anorg. Chem.*, 91, 194 (1915); *Chem. Abstracts*, 9, 3040 (1915).

[2] Richards and Willard, THIS JOURNAL, 32, 4 (1910).

It was therefore recrystallized twice from hydrochloric acid solution and fused in an atmosphere of hydrochloric acid. The recrystallization raised its melting point 7°, and probably even then it was not perfectly pure.

Caesium Chloride.—The caesium salt used had been obtained from pollucite and purified by crystallizing twice as caesium dichloriodide and twice as caesium nitrate. It was converted into the chloride by evaporation in quartz with hydrochloric acid and finally by fusing in an atmosphere of hydrochloric acid gas. It was much purer than usual.

Apparatus for Determining Freezing Points.

The Electric Furnace was constructed as follows:—A porcelain tube 50 cm. in length and with an internal diameter of 4 cm. was wound for about 30 cm. of its middle portion with two layers of ribbon of a suitable high-temperature resistance-wire, insulated by asbestos sheeting, and wrapped with this substance to prevent loss of heat by radiation. The tube was set upright in a suitable mounting. The terminals of the windings were connected with the alternating lighting circuit through a rheostat, by means of which the temperature inside the furnace could be regulated to within a few degrees. It would have been somewhat safer to fill the furnace with an inert atmosphere, but in the short time required by an experiment the oxygen of the air was found to affect the salts only very slightly, if they were thoroughly dried in the first place.

The Pyrometer.—The temperatures were measured by means of two LeChatelier thermocouples of platinum and platinum-rhodium alloy, each connected with a sensitive millivoltmeter graduated in degrees Centigrade. In order to obviate any error due to differences in temperature at the cold junctions, these were enclosed in small test tubes surrounded by melting ice and thus kept at 0°. Each pyrometer was standardized, and its readings were found to require considerable corrections, which were checked from time to time during the research. A temperature scale based upon the melting points of metals has been adopted provisionally by the Bureau of Standards at Washington. The fixed points between 300° and 1000° are the melting points of cadmium, lead, zinc, antimony, silver, copper alloy (AgCu) and silver; and the boiling point of sulfur.[1] Some of these were used, and other intermediate points, given by the melting points of stable salts easily prepared in a pure state, were also employed. These temperatures had each been determined with accuracy by several experimenters, and in each case there had been close agreement among their results.[2] The melting points of cadmium and zinc, and the boiling point of sulfur have been definitely fixed by the careful work at the Bureau of Standards. Their results agree well with

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[1] Bureau of Standards, *Circ.* 35 (Jan., 1915).

[2] See Landolt-Börnstein-Roth, "Tabellen," p. 209, *et seq.* (1912).

those obtained by investigators elsewhere. Sodium and potassium nitrates are suitable on account of the ease with which they may be purified by crystallization, and the fact that hence their freezing points are accurately reproducible. Silver chloride also is easily prepared pure. Formerly some doubt existed as to the melting point of potassium chloride. Plato has recently determined it with especial care[1] and found it to be 772.3°, which agrees closely with the values obtained at the Bureau of Standards, by Arndt, and by Lorenz and Ruckstuhl. The average of all their values is the value chosen, 773°. For sodium chloride the average value[2] 801° seems to be the most trustworthy. In the case of lead chloride, seven different values average 498° with a "probable error" of only 0.7°.[3] The three last named points, and the two alkali nitrates and cadmium are the most important for the present purpose.

In each case the substance was contained in a vessel of suitable material, hard glass in the case of sulfur and the metals, platinum or quartz in the case of the salts. The salts, with the exception of silver chloride, were purified by crystallization. Below are given the corrections to one of the pyrometers; the other gave analogous results.

THE TEMPERATURE SCALE AND PYROMETER CORRECTIONS.

Standard substance.	Fixed point.		Observed reading.	Correction.
Sodium nitrate	316° C.	M. p.	326° C.	—10° C.
Cadmium	321°	M. p.	332°	—11°
Potassium nitrate	339°	M. p.	351°	—12°
Zinc	418°	M. p.	439°	—21°
Sulfur	445°	B. p.	468°[4]	—23°
Silver chloride	451°	M. p.	475°	—24°
Lead chloride	498°	M. p.	525°	—27°
Calcium nitrate	550°	M. p.	580°	—30°
Potassium chloride	773°	M. p.	811°	—38°
Sodium chloride	801°	M. p.	840°	—39°
Sodium sulfate	875°	M. p.	916°	—41°

These corrections were plotted, and were found to be nearly linear, except at the lowest temperatures. Each reading was corrected by an appropriate quantity read off from the curve. If at any time better determinations of any of these fixed points are made, all the results given in this paper can be corrected accordingly.

The Melting Points of Lithium, Rubidium and Caesium Chlorides.

In determining the melting (or freezing) points of lithium, rubidium and caesium chlorides, the ordinary time-temperature method was used. The salt was fused in a platinum crucible in an atmosphere of hydrochloric

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[1] Plato, *Z. physik. Chem.*, **55**, 737 (1906).

[2] W. P. White, *Z. anorg. Chem.*, **69**, 327 (1910). This result is essentially like that found by the Bureau of Standards, 801° (*Circ.* **35**).

[3] See Landolt-Börnstein-Roth, "Tabellen," p. 211 (1912).

[4] Corrected for barometric pressure.

acid and, after solidifying, was removed to a stand within the furnace. The temperature of the furnace was raised until the salt was completely fused, the thermocouple, enclosed in a quartz tube of about 5 mm. internal diameter, was then inserted, and the furnace was allowed to cool. Except at the freezing point the rate of lowering was about eight or ten degrees per minute. Temperature readings were taken every quarter-minute, and from these the freezing point was readily selected, since from the time the solid phase commenced to form until solidification was complete (or almost complete), the temperature of the mass remained practically constant.

The freezing points found were as follows:

Lithium chloride	613°
Rubidium chloride	714°
Caesium chloride	645°

For the freezing point of lithium chloride Carnelley obtained the value 602° C.; Guntz, 600°; Hüttner and Tammann, 606°; Sandonini, 602°;[1] Zemczuzny and Rambach, 614°;[2] Korreng, 609°.[3] Our material was doubtless purer than that of any of the other experimenters.

Our freezing point of rubidium chloride is a good average of the best values found hitherto. Carnelley found 710° C.; Hüttner and Tammann, 712°; Sandonini, 717°; Zemczuzny and Rambach, 726°.[2] Potassium chloride *raises* the melting point of rubidium chloride.

Carnelley found the freezing point of caesium chloride to be 631°, which is probably too low. Zemczuzny and Rambach's value, 646°, is practically identical with that obtained in this investigation.[2] Korreng found 635–638°,[3] but there is no evidence that his salt was nearly as pure as ours.

Freezing Points of Binary Mixtures of the Alkali Chlorides and the Eutectic Points.

With fusions of heteromorphous solids the break in the cooling curve on the first separation of solid phase (except at the eutectic point) is

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[1] Carnelley, *J. Chem. Soc.*, **29**, 489 (1876); **33**, 273 (1878); Guntz, *Compt. rend.*, **117**, 732 (1893); Hüttner and Tammann, *Z. anorg. Chem.*, **43**, 215 (1905); Sandonini, *Rend. Linc.*, [5] **20**, I, 457 (1911). (Quoted by Landolt-Börnstein-Roth, "Tabellen," p. 220 (1912).)

[2] Zemczuzny and Rambach, *Z. anorg. Chem.*, **65**, 403 (1910). This last is an interesting research, with relative results of value. Apparently, however, the temperature scale differed from that of most other investigators by about 17° at 773°, and 18° at 800° (the melting points of potassium and sodium chlorides, respectively). If a corresponding correction is applied to the value for rubidium chloride, it would become 710°. We are inclined to think that their tendency toward high temperatures was, in the case of lithium and caesium, counter balanced by an opposite one due to heteromorphous impurity, since they do not speak of having taken especial pains to purify the salts.

[3] *Loc. cit.*

much less marked than with pure substances. This is shown by a typical cooling curve (Fig. 1) which represents an experiment with a mixture containing 12.43 grams of potassium chloride and 7.36 grams of lithium chloride, that is to say, 51 mol per cent. of the latter salt. From such a mixture potassium chloride begins to separate at about 440°, but the inflection in the curve there, although perceptible, is not at all well marked. Of course, with less rapid cooling the inflection would have been more definite. On the other hand, the eutectic point, 361°, is unmistakable. The readings of time and temperature on the cooling curve are given below:

Time.	Temp.	Time.	Temp.
0	483°	13	377°
1	471°	14	371°
2	458°	15	367°
3	448°	16	363°
4	438°	17	361°
5	433°	22	361°
6	428°	23	362°
7	420°	25	359°
8	413°	26	358°
9	406°	27	353°
10	399°	28	346°
11	392°	29	332°
12	385°		

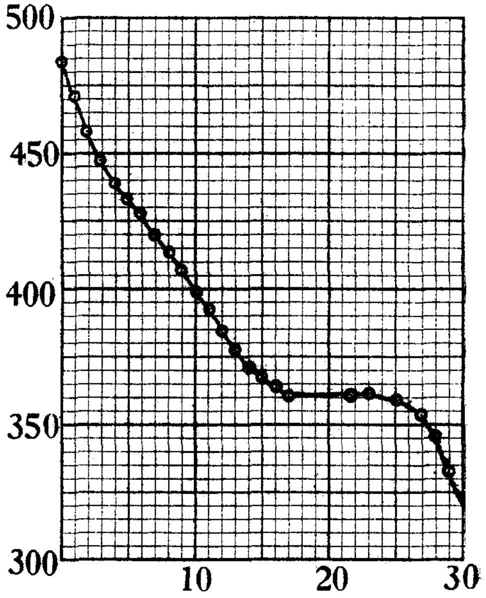

Fig. 1.

Thus the eutectic point is found to be 361°. In another entirely separate trial, with different materials and apparatus, the value 355° was obtained. The mean 358° was taken as the most probable value.

The lack of sharp definition in the cooling curve, and the probability of a slight lag in its readings, led to the adoption of another method, which, although in some respects less advantageous than the use of the cooling curve, has the advantage of being very direct and easily interpreted. This method, which gave satisfactory results, was as follows: The platinum crucible hitherto employed was replaced by one of fused silica. During a determination it was placed on a stand within the furnace consisting of a piece of large combustion tubing set upright and covered with a fused silica cap. The furnace tube itself was placed upon a glass plate, so that when the salt was fused everything within the furnace was transparent. An incandescent light, placed beneath the furnace, so increased the illumination that an observer looking from the top could see the first particles of solid that separated from the fused material. Naturally, if the salt was left undisturbed, supercooling occurred; to avoid this error the mixture was continuously agitated by stirring with the thermocouple tube, when the temperature was kept in the neighborhood of the freezing point. By careful manipulation the error from supercooling could be made very small.

Of course the concentration of the fused portion was somewhat changed by the separation of the solid, but careful adjustment reduced the error from this source to very small magnitude, as in the Beckmann method to which the present procedure was analyzed.

In a series of determinations a suitable quantity of the more stable salt (potassium, rubidium or caesium chloride) was fused, cooled in a desiccator, and weighed. Small quantities of the other constituent, lithium chloride, were added, and the mixture was rendered homogeneous and neutral by fusing in an atmosphere of hydrochloric acid gas. Subsequently it was cooled in a desiccator and the weight of lithium chloride found by difference. As the heating was very brief, but little could have been lost by evaporation.

The "freezing point" in all cases was taken to be the temperature at which the solid phase began first to appear, with suitable precautions, as the temperature fell.

The results for the freezing points of binary mixtures follow, together with the curves from which the composition and freezing points of the eutectic mixtures were determined. Each result in the following tables was obtained with a different mixture; the data have nothing to do with a time-temperature curve, except that in such a curve a break would occur at the given temperature corresponding to each mixture. The rubidium

LITHIUM CHLORIDE AND POTASSIUM CHLORIDE.

Mol. % KCl.	Mol. % LiCl.	Freezing point.	Solid phase.
100.0	0.0	773°	KCl
65.7	34.3	600°	"
60.5	39.5	552°	"
57.4	42.6	527°	"
52.2	47.8	477°	"
44.2	55.8	385°	"
42.7	57.3	367°	"
42.3	57.7	363°	"
41.5	58.5	361°	KCl + LiCl
41.3	58.7	362°	LiCl
40.6	59.4	372°	"
38.7	61.3	388°	"
35.6	64.4	412°	"
0.0	100.0	601°	"

LITHIUM CHLORIDE AND RUBIDIUM CHLORIDE.

Mol. % RbCl.	Mol. % LiCl.	Freezing point.	Solid phase.
100.0	0.0	709°	RbCl
65.6	34.4	534°	"
47.2	52.3	339°	"
46.4	53.6	327°	RbCl + $RbLiCl_2$(?)
44.8	55.2	324°	$RbLiCl_2$(?)
43.4	56.6	323°	"
42.0	58.0	320°	$RbLiCl_2$ + CiCl
41.2	58.8	327°	LiCl
30.6	69.4	455°	"
0.0	100.0	601°	"

LITHIUM CHLORIDE AND CAESIUM CHLORIDE.

Mol. % CsCl.	Mol. % LiCl.	Freezing point.	Solid phase
100.0	0.0	645°	CsCl
74.5	25.5	529°	"
63.7	36.3	442°	?
54.3	45.7	368°	?
52.0	48.0	357°	?
49.9	50.1	356°	$CsLiCl_2$
48.3	51.7	354°	"
46.2	53.8	345°	"
43.3	56.8	334°	"
38.9	61.1	339°	LiCl
32.3	67.7	407°	"
0.0	100.0	601°	"

and lithium chlorides used in these trials were not the purest at hand, but they were sufficiently pure to give a good idea of the curves. The other chlorides were from the purest samples.

These curves are interesting. On the right-hand side of the diagram we see that the addition of any one of the other chlorides to lithium chloride produces in each case very nearly the same effect for the same molal concentration, as shown by the work of Zemczuzny and Rambach, and as one might have expected. The lowering produced by caesium is somewhat greater than that by the others; on the average, 1 mol per hundred produces a depression of about 4°. Rubidium falls, as would be expected, between caesium and potassium. On the left-hand side of the diagram one notes the striking similarity of the effect of lithium chloride on the three other chlorides until as much as 25% of lithium chloride has been added. Each suffers about the same molal depression on the addition of lithium chloride as this substance suffered with each of the others. Evidently, then, the great similarity which one would expect exists on both sides of the diagram. In the middle, at the deepest points of the curves, they are markedly different. The cusp marking the eutectic point is irregular in the cases of rubidium and caesium. Not at all blunted in the case of potassium, it is considerably affected in the case of rubidium, and very much more cut off in the case of caesium. If it were not for the superposed, less steeply inclined curve, rubidium and lithium chlorides would probably have their eutectic point with about 57.8 mol per cent. of lithium chloride and about 290°, and caesium and lithium chlorides would probably have their eutectic point with about the same per cent. of lithium chloride at about 270°, as inferred from extrapolation. But the cutting off of the lower cusp quite alters the situation, and gives to the mixture of rubidium and lithium chlorides the lowest eutectic point, although this properly should fall to the lot of caesium. The only resonable explanation of this phenomenon is the assumption of the formation of a new solid phase of the type $CsLiCl_2$. The performance of rubidium

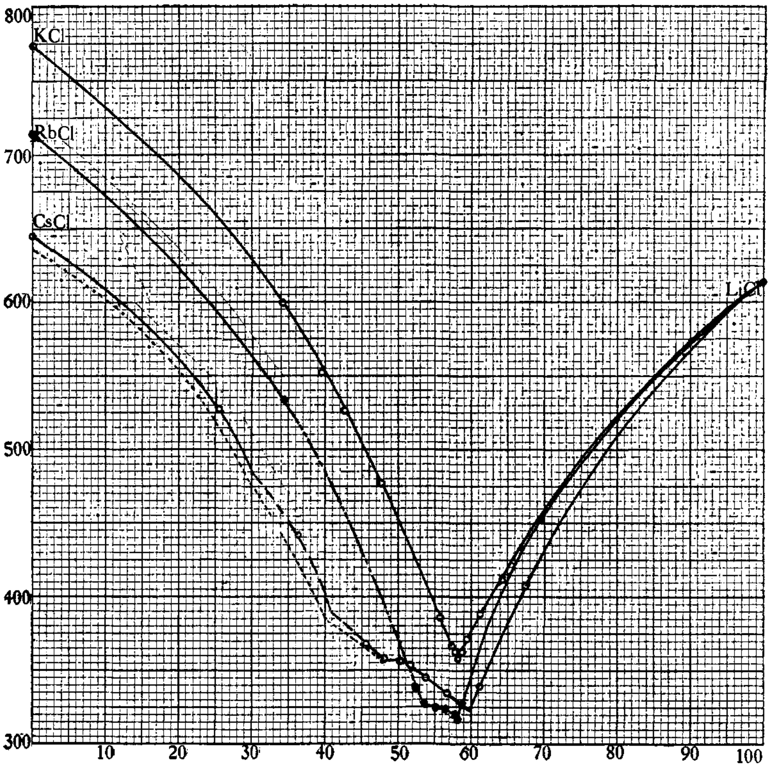

Fig. 2.—The Freezing Points of Binary Mixtures of Lithium Chloride with Potassium, Rubidium and Caesium, Respectively.

Temperatures are plotted as ordinates and molal percentages of lithium chloride as abscissae. The points for potassium and caesium chlorides are indicated by outlined circles, those for rubidium chloride by blackened circles. The lowest dotted line on the left-hand side gives Korreng's curve for caesium-lithium chloride. Those portions of our curves where the points were too few for certainty are indicated by broken lines. The lowest black circle of all represent the LiCl-RbCl eutectic point as found by the time-temperature cooling curve method.

chloride can be explained either by the assumption that RbCl.LiCl is unstable above 327°, or by the assumption that the double salt has a more complicated formula. Of these two assumptions the former seems more likely.

When the irregularity in the caesium curve was first noticed, errors of observation were suspected, and the region in question was accordingly examined again with a new mixture of chlorides, with confirmatory results. The analogous behavior of lithium and rubidium chlorides puts the matter beyond doubt. Previous investigators had not discovered this complication in the case of rubidium,[1] but the more recent work of Korreng[2] agrees essentially with our experience in the case of caesium.

The melting point of caesium chloride itself and the freezing points when mixed with 25% and 36% of lithium chloride, respectively, are a trifle higher than those found by Korreng (given by the lowest dotted line on the left-hand side of the diagram). There is good reason to believe, however, that our caesium chloride was purer than that of Korreng. Probably, therefore, the line recording our results is more nearly accurate than the lower line recording Korreng's. We did not, however, determine the slight inflections of the curves at 30% and 40% of lithium chloride. These are deduced from Korreng's curve, raising each freezing point on the diagram by approximate correction for the supposed impurity in his preparation, as indicated by the three points in our curve already mentioned.

Zemczuzny and Rambach, in their extended study of such systems, gave no details concerning their method of determining the composition of the salt mixture, nor for deciding the percentage compositions at the eutectic points. In the case of rubidium and lithium chlorides, they made no freezing-point determinations in the immediate neighborhood on either side of the eutectic point. Hence they overlooked the cutting off of the cusp of the main curve. In discussing the system CsCl + LiCl they state that at a temperature of from 355 to 360° a certain change takes place which is characterized by a transition point in the melting diagram. Probably this is the peritectic point or break in the curve indicated at 359° in our Fig. 1. They continue: "This transition is worthy of remark because it is accompanied by an intense color change. The melt solidifies on cooling, first to an opaque mass; by further cooling the formation of dark rings may be observed, which extend from the periphery to the middle. The melt becomes dark and at a content of

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[1] Zemczuzny and Rambach, *Z. anorg. Chem.*, **65**, 403 (1909); Guntz, *Z. angew. Chem.*, **158**, 1898.

[2] Korreng, *loc. cit.* This was published long after our work was finished and our main conclusions drawn.

from 20% to 30% CsCl completely black."[1] No such dark color was observed in the present research; on the contrary, the salt mixture remained pure white throughout our complete series of experiments and when fused was perfectly transparent. The color change noted by Zemczuzny and Rambach may have been due to the action of oxygen and water on their hot chlorides with the consequent liberation of chlorine and solution of the platinum of the containing vessel. This is a serious possible source of error, which might lead to mistake in the freezing point, as well as injury to either platinum or (because of the alkali) quartz vessels. It was guarded against in our experiments by fusing the salts in hydrochloric acid before each trial, as already stated.

While thus offering a different explanation for part of the observations of these authors, our work supports another conclusion of theirs and of Korreng, namely, that the caesium chloride curve contains complications between 500° and 357° which do not exist in the other curves, even although our points are too few to show all the details discovered by Korreng. It will be observed that the point at 45 mol per cent. of lithium chloride in the diagram for caesium is distinctly further to the right than it should be to correspond with those for rubidium and potassium, which the curve parallels in the upper region. According to the equation of van't Hoff ($K = 0.02T^2/MQ$) the molecular lowering is inversely proportional to the latent heat of melting. Hence the curve indicates an increase in latent heat of melting below 500°, which might be due to polymorphism in caesium chloride or the existence of a dissociable compound. Zemczuzny found the former cause; Korreng found both.

Perhaps the left-hand curve for rubidium may contain some of the complications of the caesium curve; but the fact that it parallels so well the curve for potassium (which is fairly well defined and smooth) makes this doubtful. Evidently both should be further studied in the detailed fashion followed by Korreng.

Such a phenomenon as the appearance of a solid double salt is of course familiar. Plato, for instance, observed similar behavior in the system $BaCl_2 + BaF_2$. In the melting diagram in that system there is one eutectic point corresponding to a composition of 80% barium chloride and to the freezing point 846°, and a second singular point corresponding to a composition of 30% barium chloride and to the freezing point 924°. Between the two eutectic points the double salt $BaCl_2.BaF_2$ exists as a

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[1] Korreng found 479° as the transition temperature of the two forms of caesium chloride. He found also evidence of the existence of $CsLi_2Cl_3$ with an incongruent melting point at 380°. Our data in this region are not plentiful enough to afford confirmation of this conclusion; but they do not contradict it, and Korreng's work seems to have been so careful and detailed that there is every reason to accept his outcome. Our curve is dotted in this region to show that it is incomplete.

solid phase. His curve for $CaCl_2 + CaF_2$ is even more like that for caesium, and his explanation for this case[1] applies to the system RbCl + LiCl also.

The outcome in the present case, obtained by plotting the results on a much larger scale than the published diagram, is as follows:

SINGULAR POINTS IN FREEZING CURVES OF BINARY MIXTURES WITH LITHIUM CHLORIDE.

	Peritectic point.		Eutectic point.	
Other component.	Mol. % LiCl.	Temperature.	Mol. % LiCl.	Temperature.
Potassium chloride	....	....	58.6	358°
Rubidium chloride	53.8	323°	58.3	318°
Caesium chloride	46.5	357°	59.3	323°

If any peritectic point exists in the case of potassium, the difference between it and the eutectic cannot exceed the error of observation. Korreng found the eutectic temperature for caesium chloride to be 332° with 58 mol per cent. of lithium chloride.

The compound CsCl.LiCl, indicated by the middle branch of the curve, melts at 356° or 357°;[2] on the other hand, the corresponding compound of rubidium (presumably RbCl.LiCl) must be supposed to decompose at a temperature just below its melting point, which extrapolation indicates should be about 330°. If the usual systematic relation of the heaviest three alkali metals persists in this case also, the compound KCl.LiCl should be unstable above about 305°; and hence it does not appear at all.

Freezing-Point Curves of Ternary Mixtures.

Mixtures of lithium and sodium chlorides with the chlorides of potassium, rubidium and caesium, respectively, were examined. The observations were made in the same manner as described for binary mixtures.

As the object of this series of experiments was to determine the composition and freezing point of the mixture of minimum freezing point in each system, the systems were not examined respectively over a wide range, but only in the region where this minimum point was expected.

A mixture of salts consisting of lithium chloride and caesium, rubidium or potassium chloride was made up in the proportions of the eutectic mixture and to it sodium chloride was added in weighed amounts. The freezing points of the various mixtures were determined and from the curves plotted from their values the composition of the mixture with minimum freezing point obtained by interpolation.

It is possible that the three salts might be mixed in other proportions, giving a point as low or lower than that thus found; but this is rendered improbable from the fact that the addition of lithium or potassium chloride, in the system containing these two salts with sodium chloride, to the

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[1] Plato, *Z. physik. Chem.*, 58, 362 (1907).

[2] Korreng, wholly independently, found the nearly identical value 351° (*loc. cit.*).

mixture of minimum freezing point, caused no appreciable lowering. The subject, however, admits of further study.

EUTECTIC TEMPERATURES OF TERNARY MIXTURES.

Composition: Mol per cent.			
KCl.	LiCl.	NaCl.	Freezing point.
41.4	58.6	0.0	358° C.
40.8	57.4	1.8	357°
38.9	54.8	6.3	390°
37.3	52.6	10.1	429°
39.5	41.6	28.9	550°
RbCl.			
41.7	58.3	0.0	320°
41.0	56.6	2.4	318°
39.1	54.1	6.7	328°
33.1	45.5	21.3	460°
27.3	37.6	34.9	545°
CsCl.			
41.0	59.0	0.0	325°
40.6	58.3	1.1	323°
40.3	58.0	1.7	320°
38.2	55.0	6.8	326°
37.4	53.6	9.0	354°
34.3	49.4	16.3	431°
31.2	44.7	24.1	493°

On plotting these curves it is clear that the sodium chloride produces only a very slight effect. The several eutectic points are probably about 357°, 316° and 312°, respectively. The effect of sodium chloride is least in the case of potassium and greatest in the case of caesium.

In conclusion, we are glad to express our indebtedness to the Carnegie Institution for materials and apparatus used in this research.

Summary.

1. The melting points of several alkali chlorides were found to be as follows: lithium chloride, 613°; rubidium chloride, 714°; caesium chloride, 645° (on the assumption that sodium, potassium and lead chlorides melt, respectively, at 801°, 773° and 498°). The lithium and caesium chlorides were unusually pure; but the rubidium chloride was less so.

2. The eutectic temperatures of binary mixtures were found to be as follows: potassium and lithium chlorides, 358°; rubidium and lithium chlorides, 318°; caesium and lithium chlorides, 323°.

3. The freezing curves of the last two mixtures were found to be not simple, but to contain at least one middle branch, doubtless due to a solid double salt. The similar curve apparently does not exist in the case of potassium. This middle branch was defined by Korreng in the case of caesium, but apparently has not been heretofore noticed in the case of rubidium.

4. Three eutectic ternary mixtures of lithium and sodium chlorides

with each of the three other alkali chlorides were sought in preliminary fashion, and evidence was obtained that added sodium chloride causes but little further depression of the freezing point.

[Contribution from the Department of Chemistry of Cornell University.]

THE ADSORPTION OF CARBON DIOXIDE AND AMMONIA BY CHARCOAL.

By Leon B. Richardson.

Received June 20, 1917.

The power possessed by charcoal of adsorbing in its pores large volumes of gases was first observed by Scheele, and independently by Fontana, in 1777. An extensive investigation of the process was made by Saussure[1] while various phases of the problem were studied by Joulin,[2] Kayser,[3] Chappuis,[4] and Hunter.[5] The last of these called attention to the superior adsorbing power of cocoanut charcoal, a substance utilized by Dewar many years later for the production of high vacua at the temperature of liquid air. Recently Travers,[6] Miss Homfray,[7] and Titoff[8] have treated the problem with special consideration of equilibrium conditions, and have advanced varied theories as to the nature of the adsorption process.

None of the data in the papers mentioned above extends to pressures beyond the ordinary atmospheric value. It was the object of the work described in the present article to carry the observations in the case of carbon dioxide and of ammonia to pressures of four atmospheres.

Materials and Apparatus.

The charcoal was prepared by placing fragments of cocoanut shell in an iron tube immersed in a bath of molten antimony, the temperature of which was kept near the melting point (630°). Charcoal prepared at this temperature has been found by Hunter to be most efficient as an adsorbent. Heating for one hour was found to be sufficient to drive off all volatile products. Carbon dioxide was obtained from a cylinder of the liquefied gas known to be of exceptional purity. Upon analysis 99.7% of the total volume taken was absorbed by a solution of sodium hydroxide. Ammonia was obtained from a cylinder of the liquid, the purity of which had been tested by previous work in this laboratory. The vapor pressure

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[1] Gilb, *Ann.*, **47,** 113 (1814).

[2] *Ann. chim. phys.*, **22,** 397 (1881).

[3] *Ann. Phys.*, [3] **12,** 526 (1881).

[4] *Ibid.*, [3] **12,** 160 (1881).

[5] *Phil. Mag.*, **25,** 364 (1863); **29,** 116; *J. Chem. Soc.*, **18,** 285 (1865); **20,** 160 (1867); **21,** 186 (1868); **23,** 73 (1870); **24,** 769 (1871); **25,** 649 (1872).

[6] *Proc. Roy. Soc.*, **78A,** 9 (1906).

[7] *Z. physik. Chem.*, **74,** 129 (1910).

[8] *Ibid.*, **74,** 641 (1910).